RESTRICTED ROTATION ABOUT THE ALIPHATIC CARBON-CARBON BOND

BY

ROBERT SITES VORIS

B.S., Pennsylvania State College, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINIOS, 1943

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RESTRICTED ROTATION ABOUT THE ALIPHATIC CARBON-CARBON BOND

Introduction

The phenomenon of restricted rotation has been effectively demonstrated by the work of Adams and his students on properly substituted biphenyls, aryl olefins,[1] and aryl amines. To date, however, the only evidence for restricted rotation about the aliphatic carbon-carbon bond has been furnished by thermodynamic data and by physical data on dipole moments, X-ray spectra, and Raman spectra.[2]

The purpose of the present research, therefore, was to study the preparation and resolution of compounds related to the aryl olefins but containing bulky tertiary groups in place of the aryl group. Resolution of such compounds would thus demonstrate molecular asymmetry, which could result only by the hindrance around the aliphatic carbon-carbon bond. Examination of Stuart and Fischer-Hirschfelder molecular models indicated that both the triarylcarbinyl olefins and the trialkylcarbinyl olefins should be sufficiently hindered to be resolvable; the former type was selected for the more intensive investigation.

Because of the limitations in building up structures of this type, the large part of the problem has been concerned with the search for suitable synthetic procedures.

Experimental and Discussion

The compounds toward which these investigations were directed have not been obtained, chiefly because the reactions which had been employed in the aryl olefin series[1] did not prove to be adaptable to the triarylcarbinyl analogs and because the preparation and reactions of trialkylcarbinyl ketones required special consideration.

Ethyl phenyldi-o-tolylcarbinyl ketone (I) was prepared by the following sequence: phenyldi-*o*-tolylcarbinol→phenyldi-*o*-tolylchloromethane → phenyldi-*o*-tolylacetic acid → phenyldi-*o*-tolylacetyl chloride→ethyl phenyldi-*o*-tolylcarbinyl ketone.

Procedures similar to those of Schmidlin[3] and of Whitehill[4] were followed; the use of thionyl chloride and pyridine for the preparation of triarylacetyl chlorides was a worth-while modification. The hindrance of the phenyldi-*o*-tolylcarbinyl group compares favorably with that of the mesityl group, since carbonation of the Grignard enolate of I yielded β-keto-α-methyl-γ-phenyl-γ,γ-di-*o*-tolylbutyric acid (II) which formed a stable solvate containing one and one-half molecules of benzene. Methyl phenyldi-o-tolylcarbinyl ketone, which could be prepared by the coupling of phenyldi-*o*-tolylacetyl chloride with methylmagnesium bromide but not with methylmagnesium iodide, yielded a β-keto acid which did not form a benzene solvate.

Analysis in the Grignard machine of II showed 1.75 active hydrogen atoms and the keto group should therefore be 75 per cent enolic. However, the characteristic reactions of the enol with phosphorus pentachloride and with diazomethane leading to the desired hindered olefins, β-chloro- and β-methoxy-α-methyl-γ-phenyl-γ,-γ-di-*o*-tolylcrotonic acids failed to materialize. Instead, phosphorus pentachloride converted the benzene solvate of II to the β-keto acid chloride, identical with that obtained by thionyl chloride, and further identified by analyses of the amide, anilide, and methyl ester.

Treatment of the pure β-keto acid (II) with phosphorus pentachloride gave a crystalline product containing neither halogen nor phosphorus.

With diazomethane, II yielded only the methyl ester, identical with that obtained from the acid chloride and methanol; the enol methyl ether was not produced. Presumably the difference in reactivity of this enol and those of the aroylacetic acids, which give enol ethers,[5] is explained by the fact that the latter are activated by their allylic relation to the aromatic nucleus.

Since the rearrangement of the pinacol of ethyl methyl ketone and its unsymmetrical isomer results in mixtures of isomeric ketones and since the coupling of acid chlorides with Grignard reagents leads to a variety of products, the coupling

of ethyldimethylacetyl chloride with diethylcadmium was used to prepare 4,4-dimethyl-3-hexanone. Treatment of this ketone with ethylmagnesium bromide and then with carbon dioxide or ethyl chlorocarbonate did not produce the desired β-keto acid or ester. The method of Wahlberg[6] involving bromination and conversion to the β-keto nitrile was investigated as a route to the β-chloro-γ,γ,γ-trialkylcrotonic acids, but the nonreactivity of the keto group of such β-keto nitriles and acids constitutes a serious objection to this scheme.

Exploratory Reformatsky reactions using pinacolone with ethyl bromoacetate and with ethyl α-bromopropionate confirmed the observation made by previous investigators that the isolation of the α,β-unsaturated acids would be complicated by the formation of saturated γ-lactones. The Reformatsky approach appears to be rather futile, since the tertiary ketones possessing sufficient hindrance to demonstrate restricted rotation would react as enols and fail to follow the normal course.

Ethyl acetoacetate was condensed with *t*-amyl alcohol in the presence of boron trifluoride[7] with the object of proceeding eventually to α-*t*-amyl-β-chlorocrotonic acid. This plan was discouraged by the small yield and predominance of side-reactions in the condensation. Some alkylation had occurred, however, as evidenced by ketonic cleavage and identification of 4,4-dimethyl-2-hexanone.

The utilization of 3-ethyl-3-methyl-2-pentanone, obtained by the pinacol rearrangement of 3,4-dimethyl-3,4-hexanediol, in making diethylmethyltetrolic acid is suggested as an approach to a purely aliphatic molecule exhibiting restricted rotation. Treatment of the ketone with phosphorus pentachloride followed by dehydrohalogenation,[8] carbonation of the acetylenic Grignard, and addition of one mole of bromine to the triple bond shows promise as an expeditious route to a hindered aliphatic olefin.

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Vita

The author was born in Martinsburg, West Virginia, on May 6, 1920. He received his elementary education in the public schools of Hagerstown, Maryland. In September, 1936, he entered the Pennsylvania State College from which he received the degree of Bachelor of Science in chemical engineering in June, 1940. In the fall of the same year, he enrolled in the graduate school of the University of Illinois, where he held an organic assistantship during the year 1940-1941 and the Allied Chemical and Dye Corporation Fellowship during the years 1941-1943.

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